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UNITED STATES DEPARTMENT OF AGRICULTURE CURRENT SERIAL RECORDS
AGRICULTURAL RESEARCH SERVICE
Northern Utilization Research and Development Division
Peoria, Illinois

X LINSEED OIL

Compositions for Curing Concrete X

During the past several years the Northern Division has conducted research on the use of linseed oil for coating concrete. This research included studies both on curing the concrete and for protecting concrete against scaling and spalling caused by freezing and thawing (1). Boiled linseed oil dissolved in mineral spirits is being used as an antiscalaling agent by many highway organizations (2). One phase of our utilization research was aimed at developing a linseed oil formulation that could be mixed with water at the site. Such a procedure would eliminate the hazard of a flammable solvent and would facilitate clean-up of equipment with ordinary detergent solutions. If linseed oil were applied as a curing compound shortly after the concrete was laid and if its antiscalaling effect were retained, as indicated in preliminary experiments, additional savings would result. The need to clean and dry the pavement and also to provide additional traffic control before and during application would also be avoided.

Preparation of Emulsifiable Oil: Based on our preliminary data, the composition chosen for testing combines boiled linseed oil, which possesses good film-forming properties, with three parts by weight of saturated fatty alcohols (tallow alcohols) known for their ability to retard evaporation. Three parts of tallow alcohols are added to one hundred parts of boiled linseed oil that has been previously heated to approximately 140° F. (60° C.) and the mixture is stirred. If large amounts of materials are used, the tallow alcohol should be added gradually with stirring (3). Since commercially available boiled oils vary in their emulsifying properties, we suggest that test samples of emulsifiable linseed oil be obtained from the Northern Division or other organizations that have examined the emulsifying properties of the specific sample.

Emulsion Preparation and Properties: Our emulsifiable oil (55 volume percent) is mixed with 45 volume percent of tap water. Care should be taken not to incorporate air during the mixing. In the laboratory, emulsions satisfactory for spraying are obtained by shaking the required amounts of water and oil in a bottle or by agitation with a good mixer, such as the "Premier Dispersator,"* as the oil is added to the water. The latter procedure will

*The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

improve the stability of the emulsion. This emulsion does not possess long-term stability and may have to be stirred or shaken during application to prevent separation. A satisfactory procedure is to prepare the emulsion 24 hours before use and to redisperse the oil immediately before spraying. This waiting period and redispersion is not necessary if a high shear stirrer is used like the Premier. The emulsion has spraying characteristics similar to paint but different from many solvent-thinned commercial compounds for curing concrete (3).

Application: The curing emulsion should be applied as soon as the concrete is finished (broomed, dragged, or troweled). In the laboratory, we have sprayed the emulsion on concrete using DeVilbiss perfume atomizers Nos. 15 or 16 with 15 p.s.i. air, or a DeVilbiss spray gun No. P-EGA 352E with 30 p.s.i. air. The reservoir containing the emulsion should be shaken immediately before spraying to ensure uniformity of application. Shaking or stirring of the emulsion should be repeated if the spraying operation lasts for more than 20 minutes unless the specific emulsion is known to have sufficient stability to be used for the length of time involved. In the field, we have used a DeVilbiss type MBC spray gun such as manufactured for painting. The suggested coating rate is 200 square feet per gallon of emulsion for broomed surfaces (3).

Pigmentation for Heat Reflection: In warm weather it may be desirable to incorporate white pigment in the curing compound to prevent excessive temperatures from developing in the surface of the concrete and causing failure by either thermal stress or uneven rates of curing between the surface and the bulk of the concrete. Studies designed to incorporate pigment into our emulsion are underway.

Studies on Water Loss: As part of the research, Mr. C. H. Scholer and Dr. C. H. Best of Kansas State University have investigated, under contract, the use of our linseed oil compositions for curing concrete (4). One of these compositions appears to be superior to the others according to ASTM (American Society Testing Materials) C156-55T. Their results are as follows:

Emulsion Description	Water Loss Test		ASTM C156-55T		
	Solvent or water Vol. %	Coating rate Ft. ² /gal. of emulsion	Coating wt. Lbs. of oil per yd. ²	Water loss mg/cm ² per 3 days	
None					364
Linseed O/W emulsion, 6325-51-2	50	112	0.32		49
Linseed O/W emulsion, 6325-31-5	50	112	0.32		34
Water emulsifiable linseed oil 6325-38-1	50	112 225	0.32 0.16		10 49

At our request, the Ohio River Division Laboratories, U.S. Army Engineer Division, Ohio River, tested the NU emulsifiable oil for water loss according to CRD-C302-63 "Method of Test for Sprayability and Unit Moisture Loss through the Membrane Formed by a Concrete Curing Compound," a more severe test (in our opinion). This method requires 5 replica specimens per test. The rates of application and water loss are as follows:

<u>Emulsion</u>		<u>Coating rate</u>	<u>Coating wt.</u>	<u>Water loss mg/cm²</u>	
NU oil vol. %	Water vol. %	Ft. ² /gal. of emulsion	Lbs. of oil per yd. ²	3 days	7 days
None				258	274
50	50	200	0.18	47	73
50	50	150*	0.24	32	52
55	45	200	0.20	44(63)	71(92)
55	45	150*	0.26	24	41

* CRD-C302-63 permits testing only at 200 ± 10 ft.²/gallon.

The number in parenthesis is a result obtained when two extremely high specimens were averaged in the results.

In another test using ASTM procedures, a commercial compound was compared with the emulsified linseed oil. Water-losses were 47 and 20 mg/sq.cm. at coating rates of 135 sq. ft. per gallon, respectively.

Occasional erratic results may be characteristic of some present methods of testing for water loss even though the test appears to be carried out according to the directions. Some laboratories have found losses of water after 3 days above 55 mg/cm.² when they tested our compositions. These differences may be inherent in the manner in which the materials are tested within the variables permitted. However, further testing is being undertaken.

Practical Studies on Sidewalks: We used surface treatments with our emulsifiable linseed oil and other materials to cure sections of a sidewalk laid in May 1963 in front of our building. Excellent cures with compressive strengths of from 5,000 to 6,000 p.s.i. resulted. Our examination in January 1964 disclosed a lower incidence of "pop-outs" in the areas cured with linseed oil than in the areas cured with or without other surface treatments (3).

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3. Unpublished work, Northern Utilization Research and Development Division.
4. C. H. Scholer and C. H. Best, "Linseed Oil for Curing Concrete," presented before the annual meeting of Highway Research Board, Washington, D.C., January 16, 1964.

These references contain information about the research but little detailed technical information on preparation and use of linseed oil curing and antiscaling compositions.

CA-71-27
October 1965

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PROCUREMENT SECTION
CURRENT SERIAL RECORDS

BIBLIOGRAPHY ON CORN PROCESSING

No single reference tells the story of the use of corn. Three major industries process corn: wet milling, dry milling, and fermentation. Information on these three different industrial processes appears in a few technical treatises that have become recognized as standard references. Otherwise, the information is scattered among a considerable number of articles in trade, engineering, and scientific journals. Although not exhaustive, the following bibliography brings together a number of references that describe the technology of corn processing.^{1/}

Standard Reference Books

Wet Milling

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v. I, 510 pp.; v. II, 465 pp.
John Wiley & Sons, Inc., New York, N. Y. (Each volume, \$10.00)

Dry Milling

There is no standard reference on American corn dry-milling methods, but the following review is worthy of special note in summarizing, in considerable technical detail, the knowledge on this subject:

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[See items under "corn" in index]

Journal Articles and Other References

Wet Milling

In a series of 20 articles written between 1939 and 1957, F. W. Bartling presented a detailed practical description of the equipment and processes used in wet-milling corn. During the period of writing these articles, and subsequently, centrifugal machines largely replaced the gravity tables for starch and gluten separation and the flotation tanks for germ separation described early in the series. Meanwhile, flash drying of starch and some other products has become common.

The first 12 articles by Bartling appeared in the American Miller under the general title "Wet Process Corn Milling." Starting with volume 72, January 1944, the title of the journal was changed to the American Miller & Processor, and subsequent articles were headed "Wet-Mill Process." For easier reference the subtitles of each of the 20 articles are given below:

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1952. Structure of the Mature Corn Kernel.
Cereal Chemistry
Part I. Gross Anatomy and Structural Relationships.
29 (5): 321-333.
Part II. Microscopic Structure of Pericarp, Seed Coat, and Hilary Layer of Dent Corn. 29 (5): 334-348.
Part III. Microscopic Structure of the Endosperm of Dent Corn,
29 (5): 349-361.
Part IV. Microscopic Structure of the Germ of Dent Corn.
29 (5): 362-382.

Considerable practical engineering data and information on dry- and wet-process corn milling and byproduct feed manufacture are presented in various editions of "Consolidated Catalogs," issued every 2 to 3 years. A new edition was published in 1964, somewhat changed in format and organization and with an expanded section on formula feed products for animal consumption:

(90) Consolidated Feed Trade Manual and Grain Milling Catalog. 338 pp. (\$2.00)
1964. The National Provisioner, Inc.
15 East Huron Street, Chicago, Illinois 60610

Simple flowsheets and machines required, together with advertisements of manufacturers of equipment and supplies for various types of cleaning, milling, separating, sifting, mixing, conveying, and packaging operations, are given. Of particular note is a concise flowsheet of the corn wet-milling process on page 325 of the 1964 edition and a description of the corn dry-milling process on pages 146-149 of the preceding edition which appeared as, "Consolidated Grain Milling Catalogs and Engineering Bluebook," Ed. No. 12, 1960-1961.

Another publication designed to combine practical information and extensive engineering data pertaining to the milling industry is:

(91) Association of Operative Millers
1963. Cereal Millers Handbook. 446 pp.
Burgess Publishing Company, Minneapolis, Minnesota
Available from Association of Operative Millers
639 Board of Trade Building
Kansas City, Missouri 64105
(\$12.00)

Manufacturers of equipment and supplies needed for the different unit operations of these complex production industries may also be found by consulting the various classified sections of:

(92) Thomas Register of American Manufacturers
1965. Thomas Publishing Company. Ed. 55, v. I-V
461 Eighth Avenue
New York, N. Y. 10001

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UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
Northern Utilization Research and Development Division
Peoria, Illinois 61604

PROCUREMENT ACTION
CURRENT SERIAL RECORDS

NYLON 1313

Nature of the Polyamide

Nylon 1313 is a new polyamide^{1/} that contains repeating monomer units with longer polymethylene chains than in commonly available nylons. A consequence of this structure is a moderate melting point that results in easy fabrication of the polymer for use as molding and extruding resins, adhesives, and fluidized bed coating operations. The nylon can be injection molded without use of excessive temperatures, pressures, and dwell times. It has very low water absorption and moisture regain, low mold shrinkage but high dimensional stability, good flow properties in molding applications, excellent electrical properties, and excellent resistance to attack by chemicals. Its favorably low density should be considered when comparing costs on a volume basis.

As with other polyamides, the properties of nylon 1313 polymer can be varied somewhat by the molecular weight achieved in production, the particular method of formulation, and the crystallinity achieved in fabricating specific items. The sample lot being distributed has a molecular weight of about 39,000, was pelleted by chopping of extruded rods, and contains 0.5 percent of antioxidant,^{2/} reportedly cleared by the Food and Drug Administration for use in polymers for food contact applications.

Polyamide Preparation

Nylon 1313 is readily made by conventional melt polymerization of the salt of 1,13-diaminotridecane and brassylic (tridecanedioic) acid. Both monomers can be derived in good yield from erucic (*cis*-13-docosenoic) acid, the major fatty acid in the seed oil of crambe, a new industrial oilseed crop now grown commercially in the United States. Ozonolysis of erucic acid yields the diacid monomer, brassylic acid. It in turn is converted to the dinitrile, which is then reduced to the diamine monomer, 1,13-diaminotridecane.

1/ Acknowledgment is made to personnel of the Southern Research Institute, Birmingham, Alabama, whose research, performed under contract to the Northern Division, contributed greatly in the development of this new polyamide.

2/ Ionox R 330 of Shell Chemical Company; mention of companies or products by name does not imply their endorsement by the U.S. Department of Agriculture over others not cited.

Ionox 330 now Antioxidant 330 of Ethyl Corporation, Orangeburg, South Carolina.

Processing Conditions

Although conditions given below are not necessarily optimum, they have been found workable in small-scale experiments:

Injection Molding

400° F. molding temperature, 80 p.s.i., 10 seconds molding time.

Fluidized Bed Coating

~550° F. for ~20 mil coating, thickness increases as temperature is increased (800° F. maximum). Sample rotated alternately clockwise and counterclockwise. After coating, specimen reheated in an oven to complete fusion. The adhesion of the coating to phosphate pretreated metal was stronger than the cohesive strength of the nylon.

Melt Extrusion

Film.--A 1-inch diameter Killion extruder equipped with 6 inch X 20 mil die, 435° F. in feed zone, 455° F. in metering zone, and 435° F. in die. Film was quenched in water 1/4 inch from die opening.

Rod.--A 1-inch Killion extruder equipped with 1/8-inch diameter rod die. Extruded at 375° F. at rate of 4.3 pounds per hour. Rod was quenched in water 1-1/2 inches below die.

Monofilaments.--A 3/4-inch Killion extruder equipped with 77-mil spinneret with a 4:1 L/D ratio. Extruded at 375-383° F. at 2.1 pounds per hour. Monofilament was quenched in water 4-1/2 inches from spinneret. Take-up speed was varied to change monofilament diameter.

Typical Properties of Nylon 1313

Physical Properties of Injection Molded Specimens

Specific gravity	1.01
Crystal melt temperature (DTA)	175-176° C.
Melt viscosity, poises (at 191° C.)	1,150 ^{3/}
Water absorption (immersed), %:	
After 72 hours	0.28
At equilibrium	0.75
Moisture regain, 50% RH, 25° C., %:	
After 10 days	0.18
At equilibrium	0.27
Tensile strength, p.s.i.	5,210-5,700 ^{4/}
Tensile yield strength, p.s.i.	4,640-4,660 ^{4/}
Elongation at break, %	290-130 ^{4/}
Modulus of elasticity, p.s.i.	101,000-114,000 ^{4/}
Flexural strength, p.s.i.	7,850-10,200 ^{4/}
Flexural modulus, p.s.i.	192,000-176,000 ^{4/}
Hardness, shore D	72
Impact strength, ft. lb./in.	2.6
Mold shrinkage in./in.	0.014

Chemical Resistance

The effect on tensile strength and elongation of extruded rods, immersed 8 weeks at 72° F.

Solvent	Tensile strength, p.s.i.	Elongation at break, %
None	8,710	296
5% Hydrochloric acid	8,890	306
5% Acetic acid	8,590	302
5% Sodium hydroxide	8,080	304
Xylene	8,410	258
Oil	8,200	304

^{3/} Molecular weight of this sample estimated from melt viscosity, ~39,000.

^{4/} Values on two different batches of polyamide.

Extractives

The amounts extracted (according to FDA specification 121.2502 for food packaging material) by selected solvents.

<u>Solvent</u>	<u>Extractables, % by weight</u>
Water	0.11
95% Ethyl alcohol	1.17
Ethyl acetate	0.42
Benzene	0.24
Boiling 4.2 N HCl, 1 hour	Did not dissolve

Electrical Properties

<u>Property</u>	<u>Conditioning</u>		
	<u>Dry</u>	<u>50% RH</u>	<u>Immersed</u>
Volume resistivity, ohm-cm.	8.6×10^{14}	8.5×10^{14}	1.1×10^{14}
Power factor, 10^3 c.p.s.	0.0501	0.0386	0.0661
Dielectric constant, 10^3 c.p.s.	3.05	3.10	3.15
Dielectric strength, volts/mil	2,800	2,692	2,600

Evaluation of Undrawn Film

Tensile strength, p.s.i.	7,170
Tensile yield strength, p.s.i.	5,080
Elongation at break, %	239
Modulus of elasticity, p.s.i.	164,000
Bursting strength, p.s.i./mil	0.99
Seal strength, lb./in.	2.45

Coefficient of Linear Thermal Expansion

$$\alpha = 10.3 \times 10^{-5} \text{ in./in./}^\circ\text{C. from } -30^\circ\text{ C. to } +30^\circ\text{ C.}$$

Deflection Temperature

ASTM D648-264 p.s.i.: 118° F. (48° C.)

Monofilament Tensile Properties

<u>Denier</u>	<u>Tenacity g/d</u>	<u>Elongation at break, %</u>
179	8.5	38
244	5.3	38
521	6.0	31

Potential Uses

Industrial end uses may include coatings for wire and other metals; can seam sealants; electrical insulation; molded articles, including items where high toughness is required; brush bristles and other monofilaments; gears and bearings; gaskets and sealing rings; pipes and tubing; rod stock; wrapping films; and many others. Because of its low content of extractables plus low moisture absorption, nylon 1313 has potential as a food packaging film for meat and other moisture-sensitive products where the grease-resistant property of nylon is also required. Heat sealability of films can also be accomplished at lower temperature.

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Greene, J. L., Jr., Huffman, E. L., Burks, R. E., Jr., Sheehan, W. C., and Wolff, I. A.
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CA-71-29
November 1965

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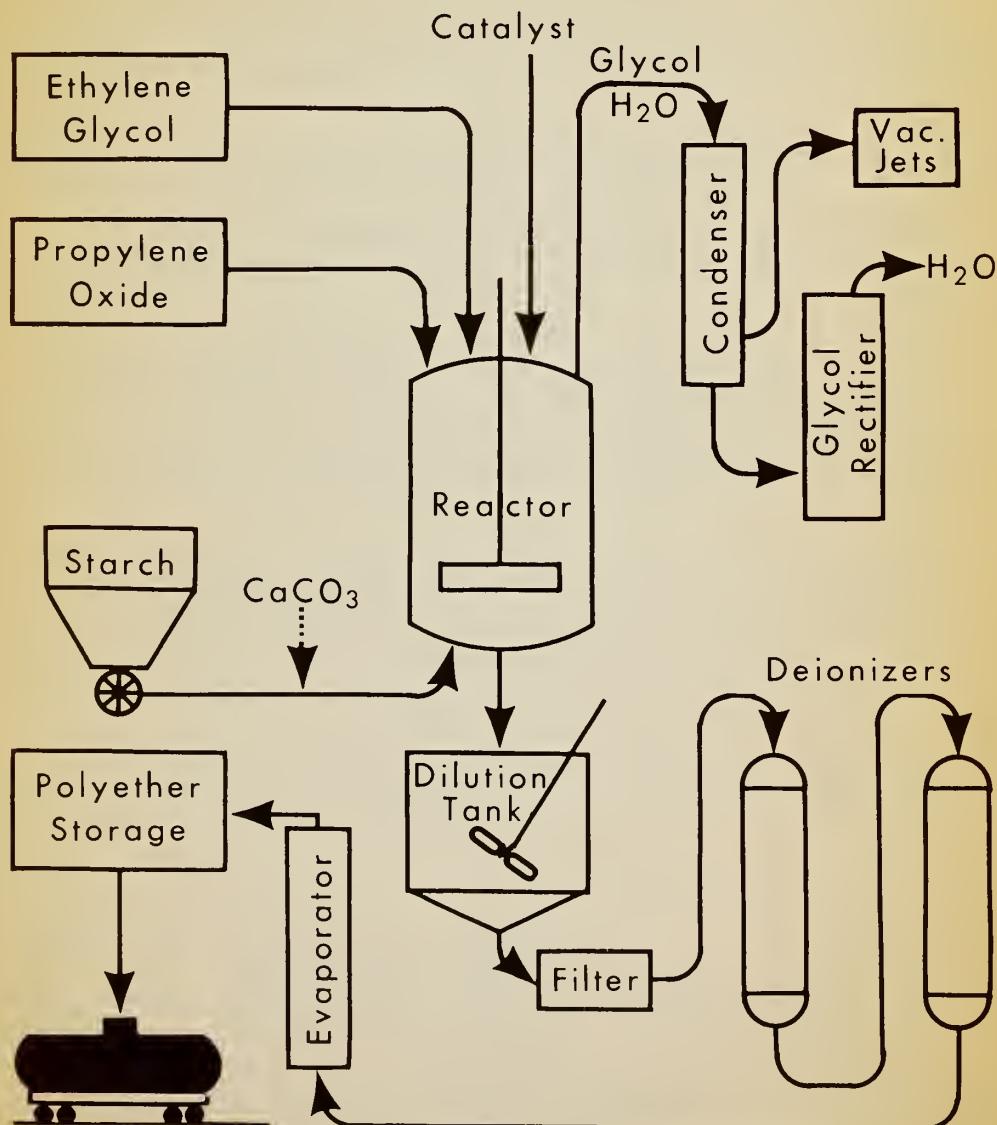
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Northern Utilization Research and Development Division
Peoria, Illinois

PROCUREMENT SECTION
CURRENT SERIAL RECORDS

STARCH-DERIVED POLYETHERS

For Rigid Urethane Foams



Flow sheet of a pilot-plant process to make starch-derived polyethers.

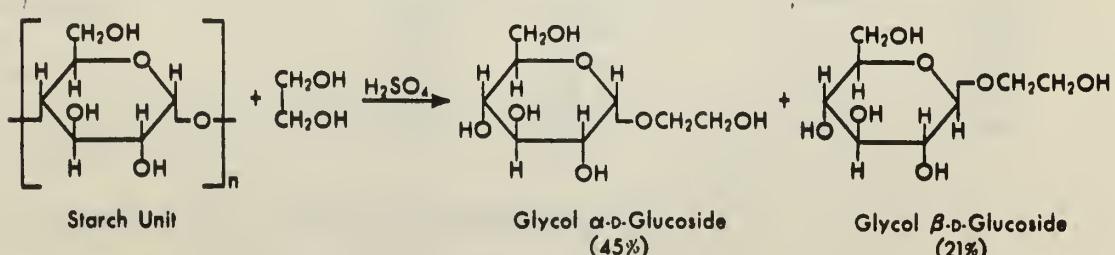
Starch-Derived Polyethers for Rigid Urethane Foams

New starch-based polyethers for use in rigid urethane foams can be made by a process developed in the Cereal Products Laboratory of this Division (1-3). A USDA research contract with Archer Daniels Midland Company (ADM) of Minneapolis, Minnesota, for the pilot plant and engineering development of the process was completed on September 30, 1965. Under this contract ADM was successful in scaling up the process to 1,000-pound batches of polyethers. Experimental rigid urethane foams with excellent properties were prepared on a foam machine pouring at the rate of 45-50 pounds per minute.

Desirable features associated with the process and products are:

1. Attractive production cost. Polyethers can be produced at a "cost to make" of about 15 cents per pound.
2. Process simplicity. A conventional reaction kettle with stirrer, cooler, heater, and a capability of withstanding 50 p.s.i.g. is adequate for polyether preparation. Moreover, all process steps, including alcoholysis and propoxylation, can be conducted in the same vessel.
3. Good product properties. Polyether viscosities are low enough that no viscosity modifiers are required. Cyclic configuration of the intermediate glycosides is believed to be responsible for good flame resistance and dimensional stability of the foams even at low polyether hydroxyl numbers.

In the process, starch is reacted with ethylene glycol to yield a mixture of glycosides (4):



+ Glycol Diglucoisides (20%) + Glycol Oligosaccharides (13%)

The glycoside mixture as made is then reacted with propylene oxide to yield polyethers. Foams are produced by crosslinking the polyethers with di- or polyisocyanates in the presence of surfactant, catalyst, and blowing agent (1).

Polyether Preparation: Into a 150-gallon kettle was charged 510 pounds of ethylene glycol and 4.25 pounds of sulfuric acid. The kettle was sealed, the charge was heated to 250° F., and the system was evacuated to 125 mm. of mercury pressure absolute. Pearl corn starch (403 pounds, dry weight) was added with stirring over a 40-minute period by allowing the starch to enter through the bottom valve of the kettle while holding the temperature at 250° F. and maintaining a pressure of 125-250 mm. of mercury absolute. After the starch was added, the charge was reacted for 45 minutes at 250° F. with a reduction of pressure to a final value of 30 mm. of mercury absolute. Calcium carbonate was then added under reduced pressure to neutralize the sulfuric acid. Potassium hydroxide (2% based on weight of glycoside) in ethylene glycol was similarly added as the etherification catalyst. Unreacted glycol was then removed at 335° F. and 4 mm. mercury pressure absolute. Total time from start of addition to end of glycol removal was 4 hours. The product contained about 1% free glycol, and 0.8 mole of glycol had reacted per unit mole of starch.

The product was then propoxylated to a hydroxyl number of about 440 by adding the calculated amount of propylene oxide over a 4-hour period at 335-365° F. and a maximum pressure of 50 p.s.i.g. The propoxylation was exothermic once initiated and required cooling to control the temperature.

The polyethers were diluted to 60% solids with water, filtered through 0.5-1% Hyflo Supercel,* deionized, and freed of water to obtain the final product.

Polyether Properties: Representative properties of pilot-plant and laboratory (3) polyethers after concentration were as follows:

Properties	Pilot plant		Laboratory	
OH Number	442	415	450**	413**
Ash, %	0.03	0.04	0.01	0.01
Water, %	0.00	0.03	0.01	0.02
pH	5.2	6.4	5-6	5-6
Viscosity, c.p.s., 25° C.	117,200	58,000	95,000	44,000

**Determined with toluene diisocyanate (5).

*The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

Polyether Cost Analysis: ADM estimates total capital cost to produce 10 million pounds per year of polyether at approximately \$375,000 for design engineering, procurement, and construction of a production unit at an existing plant site with normal services and facilities available. Plants at present equipped for propoxylation of polyols would require only a nominal conversion cost for adaptation to the new process.

Estimated "plant gate cost" of the polyether is near 15 cents per pound. This estimate is based on a raw material cost of 12.81 cents per pound of polyether. (Starch was figured at 6.1 cents per pound and propylene oxide at 14.5 cents per pound.) The labor, supervision, overhead, utilities, maintenance, insurance, taxes, and depreciation totaled 2.17 cents per pound. The low production cost is expected to give the new polyethers a cost position competitive with other polyethers.

Foam Preparation and Properties: A wide variety of formulation of B components were prepared for foaming with PAPI and Nacconate 4040 isocyanates. Two typical formulations are shown as follows:

<u>B Component</u>	<u>Parts</u>	
	<u>61B</u>	<u>61E</u>
Polyether		
OH No. 442		26.5
OH No. 415	32.0	--
Quadrol	--	6.6
R-11B	11.5	10.9
DC-113	0.5	0.5
TMBDA	0.9	--
3/1 DMEA/DABCO	--	0.5
Parts B	140	136
Parts PAPI	104	--
Parts Nacconate 4040	--	104

One-shot foam buns were prepared in a 30"x50"x10" horizontal molds in a Jennings foam machine with a rated capacity of 60 pounds per minute. Specimens were cut from the center of the buns and physical properties obtained were:

Foam No.	Density, lb./ft. ³	Closed cell, %			Comp. str., p.s.i.g.			Humid age, %ΔV	Days	K factor
					1	4	7			
61B	2.05	92	28.4		14.9	+7	+10	+10	0.114	
61E	1.95	95	42.0		18.8	+7	+7	+13	0.108	

In laboratory studies excellent foams were also obtained by using L-5320 surfactant, Mondur MR isocyanate, and dibutyl tin dilaurate catalyst.

Materials: Following is a list of reagents used in this study together with their identification and/or source:

<u>Reagent</u>	<u>Description</u>	<u>Source</u>
DABCO	Catalyst, triethylenediamine	Houdry Process and Chemical Company
DC 113	Surfactant	Dow Corning Corporation
DMEA	Catalyst, dimethylethanol amine	
Ethylene glycol	Technical grade	Silicones Division
L-5320	Surfactant	Union Carbide Corp.
Mondur MR	Isocyanate	Mobay Chemical Company
Nacconate 4040	Isocyanate	National Aniline Division Allied Chemical Corp.
PAPI	Polymethylene polyphenylisocyanate	The Carwin Company
Quadrol	Amine polyol	Wyandotte Chemicals Corporation
R-11B	Blowing Agent, CCl_3F	
Starch	Pearl corn starch	
TMBDA	Catalyst, tetramethyl butanediamine	

References

1. Rigid Urethane Foams from Glycoside Polyethers.
F. H. Otey, Bonnie L. Zagoren, and C. L. Mehlretter.
Ind. Eng. Chem. Prod. Res. Develop. 2(4): 256-259 (December 1963).
2. Degraded Starch Polyoxyalkylene Ether Compositions and Process for Producing the Same.
F. H. Otey and C. L. Mehlretter.
U.S. Patent 3,165,508 (January 12, 1965).
3. Preparation and Properties of Glycol Glycoside Polyethers for Rigid Urethane Foams.
F. H. Otey, Bonnie L. Zagoren, Florence L. Bennett, and C. L. Mehlretter.
Ind. Eng. Chem. Prod. Res. Develop., in press.

4. Separation of Isomeric Glycosides Produced by Transglycosylation of Starch with Ethylene Glycol.
F. H. Otey, Florence L. Bennett, Bonnie L. Zagoren, and C. L. Mehltretter.
Ind. Eng. Chem. Prod. Develop., in press.
5. Determination of Hydroxyl Number of Polyoxyalkylene Ethers by Reaction with Toluene Diisocyanate.
F. H. Otey, Bonnie L. Zagoren, and C. L. Mehltretter.
J. Appl. Polymer Sci. 8(5): 1985-1989 (September 1964).

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PROCUREMENT SECTION
CURRENT SERIAL RECORDS

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
Northern Marketing and Nutrition Research Division
Peoria, Illinois 61604

POWDERED ELASTOMERS

Starch Xanthide RF Encased FR-N600 (NBR)

New powdered elastomers developed at the Northern Division consist of latex particles encased in starch or flour derivatives, which are capable of serving as rubber-reinforcing agents. A wide variety of compositions are possible. Selected powdered elastomer compositions have been prepared on a pilot-plant scale.

Powdered elastomers offer substantial savings to rubber processors because they can be fabricated into rubber articles by powder processing techniques common in the plastics industry. All ingredients of a compounding's recipe can be premixed in a high-intensity Henschel-type mixer to give a free-flowing powder mix. The premix compound can then be fed directly to an extruder or injection molding machine to achieve high-speed automated production of rubber goods. Alternatively, existing processes and equipment may be adapted to permit use of premix compounds with large savings in processing costs. In addition to these savings, an estimated savings in capital investment of more than 50 percent can be realized by designing new rubber fabrication plants for powder in place of baled elastomers.

The following data describe an economical powdered NBR elastomer designed as a base for oil-resistant rubbers:

Cost

Estimated Cost to make as of June 1970 (Based on an elastomer cost of \$0.485/lb.)	\$0.469/lb.
---	-------------

Composition

FR-N600 elastomer	100.00 parts
Starch xanthide, starch basis	18.10
Resorcinol-formaldehyde	0.75
Antioxidant, nonstaining types	2.45
Stearic acid	1.00
Hi Sil 215	4.80
Total	127.10 parts

Properties

ML 1+4 (100° C.)	74
Particle size	
Through 8 mesh screen	98.1%
Through 20 mesh screen	67.1%
Through 30 mesh screen	35.1%

Test Recipe

The powder contains enough antioxidant and stearic acid for most applications. A typical test recipe is as follows: Powder masterbatch 127.1 parts, non-staining antioxidant 1.0 part, zinc oxide 5.0 parts, sulfur 2.0 parts, benzo-thiazyl disulfide 1.5 parts, tetramethylthiuram disulfide 0.1 part, and variable fillers.

Processing

In laboratory testing, a Waring Blender duplicates the mixing action of larger scale Henschel-type mixers. Usual time for mixing is only 30 seconds at high speed. For development of maximum vulcanizate properties, a small amount of additional shear mixing is needed. In laboratory testing, such mixing is obtained by passing through a tight nip on a differential roll mill for up to three passes; or by a single extrusion from a 10:1 (length-to-diameter) ratio rubber extruder.

Vulcanizate Properties

The response of the powdered elastomer to addition of conventional fillers and reinforcing agents is indicated by data in Table I. More detailed compounding studies are in progress.

References

Specific details on production of this powdered elastomer and other compositions are available. Two general references are pertinent:

Goshorn, T. R., Jorgenson, A. H., and Woods, M. E., "Powdered Rubber Technology. I. Processing Powdered NBR Compounds." *Rubber World*, 161, 66-72, October 1969.

Buchanan, R. A., Katz, H. C., Russell, C. R., and Rist, C. E., "Starch In Rubber. Powdered Elastomers from Starch-Encased Latex Particles." Presented at the 98th meeting of the Division of Rubber Chemistry, ACS, Chicago, Illinois, October 20-23, 1970. Preprints available.

The information presented is believed to be accurate but carries no guarantee or responsibility on the part of this Division. None of this information can be taken as recommendation to use the materials described in violation of patents. Mention of firm names or commercial products does not constitute an endorsement by the U.S. Department of Agriculture.

Table I. Effect of Added Fillers on Properties of Vulcanizates
from Starch Xanthide-RF Encased FR-N600 Powder

Property	Hard clay, phr			Hydrated silica, phr			HAF black, phr			
	None	26	52	78	20	40	60	18	36	54
Cure time at 150° C., min.	13	12.5	13	16	8	11.5	13	10.5	10	9.5
Specific gravity	1.10	1.21	1.31	1.39	1.16	1.23	1.28	1.16	1.20	1.24
Hardness, Shore A	78	76	80	85	80	89	97	77	84	90
Resilience, %	23	19	18	20	23	25	28	25	21	21
300° Modulus, psi	940	1200	1380	1640	1100	1300	1780	1500	2360	--
Tensile strength, psi	1450	1900	2140	2300	1940	2560	3120	1760	2900	3180
Ultimate elongation, %	430	490	500	510	500	530	520	370	360	290
Set at break, %	21	35	46	62	30	48	62	18	25	22
Tear resistance, lb./in.	210	245	282	282	283	385	434	234	304	310
Compression set, B, %	32	42	41	42	55	49	61	34	25	27
Abrasion rate, cm. 3/hr.	0.018	0.020	0.81	0.92	0.006	0.012	0.015	0.037	0.084	0.084
After 70 hr. of water immersion at 70° F.:										
Volume swell, %										
Tensile strength, psi	670	930	1860	2050	1100	1920	2390	990	2300	2640
Elongation, %	430	510	650	640	490	630	610	320	380	320

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Northern Marketing and Nutrition Research Service
Peoria, Illinois 61604

POWDERED ELASTOMERS

Zinc Starch Xanthate RF Encased SBR 1511

New powdered elastomers developed at the Northern Division consist of latex particles encased in starch or flour derivatives which are capable of serving as rubber-reinforcing agents. A wide variety of compositions are possible. Selected powdered elastomer compositions have been prepared on a pilot-plant scale.

Powdered elastomers offer substantial savings to rubber processors because they can be fabricated into rubber articles by powder processing techniques common in the plastics industry. All ingredients of a compounder's recipe can be premixed in a high-intensity Henschel-type mixer to give a free-flowing powder mix. The premix compound can then be fed directly to an extruder or injection molding machine to achieve high-speed automated production of rubber goods. Alternatively, existing processes and equipment may be adapted to permit use of premix compounds with large savings in processing costs. In addition to these savings, an estimated savings in capital investment of more than 50 percent can be realized by designing new rubber fabrication plants for powder in place of baled elastomers.

The following data describe a low-cost, nonstaining SBR powdered elastomer designed for general-purpose utility:

SBR 1511 Powder

Cost

Estimated Cost to make as of June 1970 \$0.202/lb.
(Based on an elastomer cost of \$0.1959/lb.)

Composition

SBR 1511 elastomer	100.00	parts
Zinc starch xanthate, starch basis	30.00	
Zinc, as zinc oxide	5.00	
Resorcinol-formaldehyde	1.10	
Antioxidant, nonstaining types	1.25	
Stearic acid	1.00	
Hi Sil 215	9.00	

Total 147.35 parts

Properties

ML 1+4 (100° C.)	115
Particle size	
Through 8 mesh screen	100.0%
Through 20 mesh screen	97.8%
Through 30 mesh screen	87.3%
Through 40 mesh screen	47.9%

Test Recipe

The powder contains enough antioxidant for some applications and enough stearic acid and zinc for cure activation. A typical test recipe is as follows: Powder masterbatch 147.35 parts, stain-resistant naphthenic oil 10 parts, nonstaining antioxidant 1.0 part, sulfur 2.0 parts, benzothiazyl disulfide 1.5 parts, tetramethylthiuram disulfide 0.1 part, and variable fillers.

Processing

In laboratory testing, a Waring Blender duplicates the mixing action of larger scale Henschel-type mixers. Usual time for mixing is only 30 seconds at high speed. For development of maximum vulcanizate properties, a small amount of additional shear mixing is needed. In laboratory testing, such mixing is obtained by passing through a tight nip on a differential roll mill for up to three passes; or by a single extrusion from a 10:1 (length-to-diameter) ratio rubber extruder.

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Table I. Effect of Added Fillers on Properties of Vulcanizates
from Zinc Starch Xanthate RF Encased SBR 1511 Powder

Property	No added filler		Hard clay, phr			Hydrated silica, phr			HAF black, phr		
	Without plasticizer ^{1/}	With plasticizer	26	52	78	20	40	60	18	36	54
Cure time at 150° C., min.	25	20	37.5	37	41	18	38	45	20.5	21	21
Specific gravity	1.093	1.095	1.189	1.278	1.353	1.154	1.202	1.251	1.141	1.155	1.217
Hardness, Shore A	73	72	83	87	76	88	98	77	86	90	90
Resilience, %	46	41	36	33	38	33	31	39	33	28	28
100% Modulus, psi	460	440	480	600	700	380	440	560	570	740	900
300% Modulus, psi	1240	1170	1250	1330	1420	980	1000	960	1680	2240	2670
Tensile strength, psi	1970	2060	2180	2400	2090	2050	2440	1840	2680	2820	2830
Ultimate elongation, %	470	540	570	620	520	580	670	670	490	380	320
Set at break, ^{1/}	45	30	50	90	80	55	90	130	35	35	50
Tear resistance, lb./in.	171	181	224	248	277	250	299	242	272	276	261
Compression set, B, %	25.6	20.6	22.9	28.3	29.8	28.4	44.7	82.6	21.9	22.3	22.6
Abrasion rate, cm.3/hr.	0.105	0.198	0.868	1.137	1.488	0.269	0.263	0.254	0.140	0.159	0.159
After 70 hr. of water immersion at 70° F.:											
Volume swell, %	15.8	12.1	6.7	4.4	3.3	7.8	4.7	3.8	7.4	6.0	4.1
Tensile strength, psi	650	580	1080	1600	1500	810	1720	1580	1460	2040	2160
Elongation, %	510	410	520	610	530	490	620	660	400	350	290

^{1/} All other compositions contained 10 phr stain-resistant naphthenic oil as plasticizer.

CA-71-34
3 January 1971

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PROCUREMENT SECTION
CURRENT SERIAL RECORDS

POWDERED ELASTOMERS

Zinc Starch Xanthate Encased SBR 1713

New powdered elastomers developed at the Northern Division consist of latex particles encased in starch or flour derivatives which are capable of serving as rubber-reinforcing agents. A wide variety of compositions are possible. Selected powdered elastomer compositions have been prepared on a pilot-plant scale.

Powdered elastomers offer substantial savings to rubber processors because they can be fabricated into rubber articles by powder processing techniques common in the plastics industry. All ingredients of a compounding's recipe can be premixed in a high-intensity Henschel-type mixer to give a free-flowing powder mix. The premix compound can then be fed directly to an extruder or injection molding machine to achieve high-speed automated production of rubber goods. Alternatively, existing processes and equipment may be adapted to permit use of premix compounds with large savings in processing costs. In addition to these savings, an estimated savings in capital investment of more than 50 percent can be realized by designing new rubber fabrication plants for powder in place of baled elastomers.

The following data describe a low-cost, nonstaining, oil-extended, powdered SBR elastomer designed for general-purpose utility:

SBR 1713 Powder

Cost

Estimated Cost to make as of June 1970 \$0.166/lb.
(Based on an elastomer cost of \$0.1959/lb.)

Composition

SBR 1713 elastomer	100.00 parts
Sunthene 3120 oil	50.00
Zinc starch xanthate, starch basis	30.00
Zinc as zinc oxide	4.35
Antioxidant, nonstaining types	1.50
Stearic acid	1.50
Hi Sil 215	<u>14.25</u>
Total	201.60 parts

Properties

ML 1+4 (100° C.)	55
Particle size	
Through 8 mesh screen	94.0%
Through 20 mesh screen	64.0%
Through 30 mesh screen	36.5%

Test Recipe

The powder contains stearic acid and zinc as oxide for activation of sulfur-accelerator cure, and enough antioxidant for many applications. A typical test recipe is as follows: Powder masterbatch 134.4 parts, nonstaining antioxidant 1.0 part, sulfur 2.0 parts, benzothiazyl disulfide 1.5 parts, tetramethylthiuram disulfide 0.2 part, and variable fillers.

Processing

In laboratory testing, a Waring Blender duplicates the mixing action of larger scale Henschel-type mixers. Usual time for mixing is only 30 seconds at high speed. For development of maximum vulcanizate properties, a small amount of additional shear mixing is needed. In laboratory testing, such mixing is obtained by passing through a tight nip on a differential roll mill up to three passes; or by a single extrusion from a 10:1 (length-to-diameter) ratio rubber extruder.

Vulcanizate Properties

The response of the powdered elastomer to addition of conventional fillers and reinforcing agents is indicated by data in Table I. More detailed compounding studies are in progress.

References

Specific details on production of this powdered elastomer and other compositions are available. Two general references are pertinent.

Goshorn, T. R., Jorgenson, A. H., and Woods, M. E., "Powdered Rubber Technology. I. Processing Powdered NBR Compounds." *Rubber World*, 161, 66-72, October 1969.

Buchanan, R. A., Katz, H. C., Russell, C. R., and Rist, C. E., "Starch In Rubber. Powdered Elastomers from Starch-Encased Latex Particles." Presented at the 98th meeting of the Division of Rubber Chemistry, ACS, Chicago, Illinois, October 20-23, 1970. Reprints available.

The information presented is believed to be accurate but carries no guarantee or responsibility on the part of this Division. None of this information can be taken as recommendation to use the materials described in violation of patents. Mention of firm names or commercial products does not constitute an endorsement by the U.S. Department of Agriculture.

TABLE I. Effect of Added Fillers on Properties of Vulcanizates
from Zinc Starch Xanthate Encased SBR 1713 Powder

Property	Hard clay, phr				Hydrated silica, phr				HAF black, phr			
	None	26	52	78	10	30	50	18	36	54		
Cure time at 150° C., min.	15.5	21	28	22	12.5	22	24	24.5	22	16		
Specific gravity	1.08	1.19	1.29	1.37	1.13	1.19	1.23	1.14	1.19	1.22		
Hardness, Shore A	48	53	62	67	49	68	83	60	70	75		
Resilience, %	51	47	40	35	49	38	29	40	29	26		
300% Modulus, psi	425	420	600	600	410	660	820	920	1360	1740		
Tensile strength, psi	1180	1430	1640	1580	1320	1730	1840	1800	2130	2130		
Ultimate elongation, %	725	760	710	750	730	750	680	560	480	390		
Set at break, %	22	50	72	100	25	50	65	30	30	20		
Tear resistance, lb./in.	153	180	203	203	165	221	332	201	230	201		
Compression set, B, %	25	34	39	51	24	46	57	23	25	25		
Abrasion rate, cm.3/hr.	3.01	3.19	1.75	2.10	3.05	1.04	0.44	0.83	0.48	0.31		
After 70 hr. of water immersion at 70° F.:												
Volume swell, %	5.7	2.4	4.3	2.9	2.7	3.4	3.6	3.0	2.3	2.1		
Tensile strength, psi	520	760	1420	1040	1280	1640	1310	1500	2050	1540		
Elongation, %	530	760	800	800	670	790	720	520	490	380		

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CA-71-36
June 1972

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE 23 '71
Northern Regional Research Laboratory
Peoria, Illinois 61604

CRAMBE

CURRENT USES

Nature of the Crop

A member of the mustard family (Cruciferae), the crambe plant grows about 3 feet tall and produces a great number of seeds borne singly in spherical pods or hulls. Flowering is indeterminate, but the early formed pods usually adhere until later ones mature (11). As of June 1972, two named varieties, Prophet and Indy, are available--both released by the Purdue Agricultural Experiment Station, Lafayette, Indiana. Prophet is a selection from Crambe abyssinica; Indy is from Crambe hispanica. A major advantage claimed for Indy over Prophet is a shorter growing time--75 to 80 days vs. 90 days to maturity. In some regions, domestic production of two crops per year may be feasible. As harvested, so-called seed of both varieties contain about 30 percent pericarp and 31-32 percent oil. Dehulling leaves the true seed whose oil content is approximately 45 percent (1). Current yields of seed-plus-pericarp are around 1,000 to 2,000 pounds per acre; further increases are anticipated as new varieties are developed and cultural practices are improved.

Traditionally, U.S. companies requiring erucic acid and oil containing it have been dependent upon rapeseed-growing countries for raw material. Current trends in most of these countries toward production of low-erucic rapeseed varieties for improved nutritional quality of the oil have increased the importance of crambe as a domestic source of high-erucic oil for nonedible industrial purposes (10).

Composition and Properties of the Seed Oil

The triglyceride oil from crambe seed resembles that from ordinary rapeseed in composition but contains higher and more consistent levels of esterified erucic (*cis*-13-docosenoic) acid. A valuable commercial product *per se*, this 22-carbon monounsaturated acid also imparts useful properties to the oil. Viscosity, density, and smoke point of crambe oil are higher than for other domestic vegetable oils. Composition and properties typical of refined and bleached crambe oil (5) are as follows:

<u>Composition, Percent</u>		<u>Physical and Chemical Properties</u>	
Erucic acid	55-60	Specific gravity, 25/25° C.	0.908
Oleic acid	15	Viscosity, 25° C., cp.	85
Linoleic acid	10	Viscosity, 25° C., Gardner	C
Linolenic acid	7	Refractive index, 20° C.	1.472
Eicosenoic acid	3	Refractive index, 40° C.	1.466
Palmitic acid	2	Gardner color	1-3
Behenic acid	2	AOCS color (spectrophotometric)	2.4
Tetracosanoic acid	3	Melting point, °C.	6 (43° F.)
Free fatty acids	0.2	Iodine value	93
Unsaponifiables	0.5	Smoke point, °C.	271 (520° F.)

Market Opportunities

Triglyceride Oil

The long hydrocarbon chains of the erucic groups in crambe oil impart efficacy in lubricant uses. In one of the more novel applications, leading steel producers have found crambe oil to be superior to other oils as a mold lubricant in the continuous casting of steel (8). It should also be beneficial in formulated lubricants, since addition of high-erucic triglycerides to mineral oil is known to increase "oiliness" of base stock and to improve durability under high-speed and high-pressure operations.

Like other unsaturated vegetable oils, crambe oil may be vulcanized by reaction with sulfur or sulfur derivatives. The familiar art gum eraser is made of vulcanized vegetable oil. In larger volume markets, vulcanized vegetable oils are blended with natural and synthetic rubbers to facilitate processing, to provide soft elastic products with improved resistance to light and ozone, and to increase tolerance toward liquid plasticizers. A vulcanized product made from crambe oil has given excellent results in commercial evaluation (8).

Fully hydrogenated crambe oil is glossy and waxlike and has a Brinell hardness number of 1.1 as compared to 0.24 for paraffin (3).

Erucic Acid Derivatives

Erucamide, probably the most important commercial derivative of erucic acid, is at present considered one of the best additives for extruded polyethylene and polypropylene film (8). When added to virgin polyolefin resins in low concentrations (ca. 0.1%), this amide functions as an extruder lubricant during processing. In addition, it exudes to the film surfaces and acts as an antiblocking and slip-promoting agent in the finished product; i.e., it prevents films from adhering to one another and allows sheets to slide past each other easily. Due to its low volatility, erucamide is especially recommended where high temperatures are involved; it is the preferred amide for use with polypropylene, even though currently more expensive than aliphatic amides with shorter chains (e.g., oleamide).

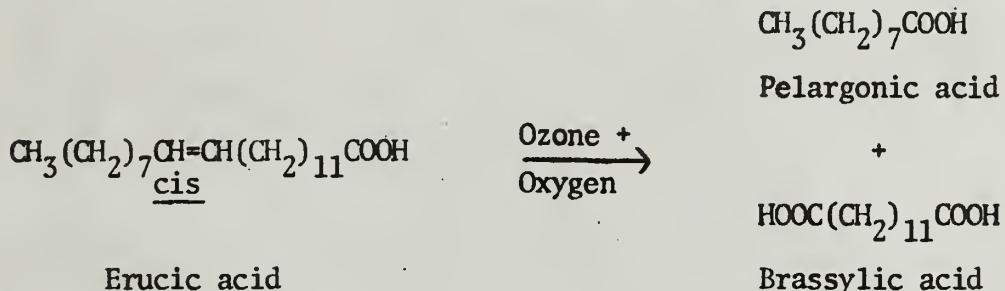
Behenyl amine, the 22-carbon saturated amine from erucic acid, is an effective agent in fabric softeners, emulsifiers, corrosion inhibitors, and in other familiar applications of long-chain cationic surfactants.

Several N,N-disubstituted amides of erucic acid and mixed crambe fatty acids can be prepared by amidation of the free acids or by direct aminolysis of the triglycerides (4). Potentially useful in many ways, these amides performed quite well when specifically evaluated as plasticizers.

Liquid wax esters prepared chemically from crambe oil are prospective sperm whale oil replacements. These esters and other derivatives exemplify the objectives of current research on erucic acid and the total mixture of crambe fatty acids.

Products from Cleavage of Erucic Acid

Oxidative ozonolysis of erucic acid produces a monobasic acid, pelargonic, and a dibasic acid, brassyllic, according to the following equation:



Pelargonic acid enjoys an excellent market, mainly in the manufacture of synthetic lubricants for jet aircraft engines.

Uses of brassyllic acid are many and varied. For example, its cyclic diester with ethylene glycol, ethylene brassylate, is a well-known synthetic musk employed as a fixative in perfumes.

A new polyamide (nylon 1313) made from brassyllic acid and the corresponding diamine has repeating units with longer uninterrupted polymethylene chains than other nylons (2). A moderate melting point and exceptionally low water absorption are consequences of this structure. Nylon 1313's melt characteristics are desirable in adhesives and facilitate fluidized-bed coating, molding, and extrusion; its low moisture affinity contributes to excellent electrical properties and dimensional stability (9).

Alkyl diesters of brassyllic acid, or of the mixed dibasic acids made from ozonolysis of total crambe free fatty acids, are excellent low-temperature plasticizers for poly(vinyl chloride) (6,7).

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